Short communication

1,2,4,5-Tetramethoxybenzene as a redox shuttle and their analogues in Li-ion batteries

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HIGHLIGHTS

► 1,2,4,5-tetramethoxybenzene derivatives as electrode material for Li-ion batteries.
► Quinonic structures showed a better electrochemistry compared to hydroquinonic.
► Double methylation results in a lower electrochemical potential.
► Redox shuttle at a potential of 3.6V versus metallic lithium.

ABSTRACT

Five different analogues of 1,2,4,5-tetramethoxybenzene were prepared and characterised for their potential use in Li-ion batteries. The samples constitute two pairs of substituted redox quinone/hydroquinone samples and a 1,2,4,5-tetramethoxybenzene sample. More specifically, the first pair was 2,5-hydroxy-substituted (non-methylated) quinone whereas the second one was 2,5-methoxy-substituted (double methylated). The quinonic structures showed a better electrochemical stability in Li-ion environment compared to the hydroquinonic structures that showed large irreversible consumption of charge during the first oxidation. Double methylation of quinone led to organic molecules with electrochemical activity at lower potential. Although non-methylated and double methylated quinonic molecules can reversibly exchange two electrons, the observed capacity was lower and only the double methylated sample showed a two-plateaux behaviour. The 1,2,4,5-tetramethoxybenzene sample that showed a formation of radical cation at a potential of 3.6 V versus metallic lithium was tested as a shuttle molecule in a combination with a $LiFePO_4$ cathode material. The results indicate that this molecule can probably effectively prevent overcharging of batteries based on the $LiFePO_4$ cathode material.

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1. Introduction

Lithium ion batteries are penetrating into everyday life through different applications. Certain emerging active in Li-ion batteries materials show very promising electrochemical performance but for use on larger practical scales their synthesis is often energetically unfavourable thus leading to hardly acceptable costs. Among different less energetically demanding possibilities organic molecules may represent an interesting alternative. They can be prepared with a large variety of possible atom arrangements and this gives a possibility for tuning their structure and composition into interesting classes of active materials with different properties.

Even small changes in the structure can induce considerable changes in the electrochemical activity, redox potential, as well as stability. However from the available research reports it seems that there are still major limitations that are preventing the commercial use of organic molecules in batteries. One of them is their solubility in the aprotic electrolytes typically used in Li-ion battery research [1,2]. This problem can be overcome by grafting/attaching of active species on non-soluble substrate. This way, stable cycling can be obtained, however the energy density is decreased to the degree where competition with inorganic materials becomes very difficult. The third problem is their thermodynamic and kinetic properties which, in most cases, leads to slow and irreversibly electrochemistry at potentials above 4 V versus lithium reference. Still, the large variety of organic molecules offers almost infinite number of combinations and with innovative approach it is possible to isolate

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some active materials that can have a potential to be used in realistic energy storage systems.

Quinone based materials were early recognized as potential electrode materials [3,4]. The theoretical capacity of the simplest quinone derivate, 1,4-benzoquinone, is close to 500 mAh g^{-1} since a two electron reaction can be expected. Later on, the use of 2,5-dihydroxybenzoquinone analogues such as lithium chloroanilate (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) [5] or polymer (Poly(2,5-dihydroxy-1,4-benzoquinone-3,6-methylene)) [6] has been suggested. In other studies, lithium chloroanilate has delivered capacities of about 200 mAh g^{-1} ($\sim$80% of the theoretic value) at around 2 V vs. Li. Again, the cycling stability was poor (50% loss after 25 cycles). Another polymer (Poly(2,5-dihydroxy-1,4-benzoquinone-3,6-methylene)) [6] compound showed improved cycling stability ($\sim$20% loss after 100 cycles due to lower solubility of the polymer in electrolyte), but a decreased performance of 140 mAh g^{-1} (40% of the theoretical value) at around 2.2 V vs. Li.

The stability of quinone derivatives in Li-ion electrolytes can be improved by grafting or by tuning their structure. In this study we focus on oxidized and/or methylated derivatives of 1,2,4,5-tetrahydroxybenzene. Five different quinonic/hydroquinonic structures and their hydroxy/methoxy derivatives (Fig. 1) are checked for their potential use in Li-ion batteries. Electrochemistry of some samples in this study was published before [1,7], here we compare difference between oxidized and reduced state of hydroxy/methoxy derivatives. Complete methylation of the 1,2,4,5-tetrahydroxybenzene led to compound, in which electrochemical activity was initially not expected at all. However, it is shown that the formation of a stable radical cation during oxidation of 1,2,4,5-tetramethoxybenzene in combination with its solubility in the electrolyte can be used as a redox shuttle for overcharge protection of a LiFePO$_4$ cathode material. To our best knowledge this is the most suitable redox shuttle molecule among reported molecules [8–12] for the overcharge protection of LiFePO$_4$ based batteries.

2. Experimental

The reaction conditions for the synthesis procedure from quinone **HQ** to its methylated and reduced derivatives are shown in Fig. 1. 1,2,4,5-Tetrahydroxybenzene (**HB**) was synthesized by reduction of quinone **HQ** (7.0 g, 50 mmol) with tin (7.13 g, 60 mmol) and 37% HCl (152 mL, 1.8 mol) as described elsewhere [13]. Recrystallization with THF gave only poor yields (2.61 g, yield 37%) unless we cool down the solution to low temperature -100 °C (5.6 g, yield 79%). The purity and composition was checked by ^{1}H NMR and IR (KBr $-$ pellet), the results were in agreement with previous work [13].

1,2,4,5-Tetramethoxybenzene (**MB**) was prepared from **HB** (1.9 g, 13.4 mmol) and K$_2$CO$_3$ (11.2 g, 81 mmol) that were suspended in acetone (25 mL) under argon atmosphere. After addition of dimethyl sulphate (10.2 g, 81 mmol) through septa, the solution was stirred and refluxed for 12 h, followed by evaporation of solvents. The obtained powder was suspended in water and extracted with dichloromethane. Organic phase was dried with Na$_2$SO$_4$, evaporated and the brownish product was recrystallized in boiling THF followed by cooling to low temperature (-78 °C). The crystals were filtered, washed again with a small amount of cold (-78 °C) THF and dried (1.72 g, yield 65%). The purity and composition was checked by ^{1}H NMR, the results were in agreement with previous work [14].

2,5-Dimethoxy-1,4-benzoquinone (**MQ**) was prepared by suspending **HQ** (6.59 g, 47 mmol) in MeOH (350 mL, 8.6 mol) with 30 mL of concentrated HCl and stirred at room temperature overnight [15]. The precipitate was filtrated, washed with cold MeOH and dried (7.2 g, yield 91%). The purity and composition was checked by ^{1}H NMR, the results were in agreement with previous work [16].

1,4-Dihydroxy-2,5-dimethoxybenzene (**HMB**) was prepared by suspending **MQ** (3.36 mg, 20 mmol) in a mixture of water (300 mL) and of MeOH (150 mL) under argon atmosphere followed by addition of sodium dithionite (10.4 g, 60 mmol) [17]. The mixture was stirred for 1 h to become colourless. Solution was dried by evaporation of methanol under reduced pressure and the product was extracted twice. Organic phase was dried with Na$_2$SO$_4$, evaporated under reduced pressure and the solid product was stored in the freezer (2.4 g, yield 71%). The purity and composition was checked by ^{1}H NMR, the results were in agreement with previous work [17].

Electrochemically active composites were prepared by mixing organic active material with carbon black (Ketjenblack, ECP-600JD) in a ratio of 1:1. The formed composite (83%) was further homogenised with a solution of Ethylene-Propylene-Diene Monomer Rubber (EPDM) in hexane (17%) by using a mortar and pestle. To prepare the electrodes, the slurry was transferred onto several Al current collectors (2 cm^2 surface area) and left to dry at room temperature. The electrodes were then transferred and kept in a glovebox ($<$1 ppm water) for at least 24 h before use. "Coffee bag" batteries were assembled in which the working electrodes were the composites with organic molecules, while a lithium foil served as a counter electrode. The electrodes were separated with a glass wool separator soaked with 1 M solution of LiPF$_6$ in a mixture of ethylene carbonate/diethyl carbonate (EC/DEC = 1:1).

The electrochemical measurements were conducted using a VMP3 potentiostat/galvanostat (Bio-Logic, France). The current density in the galvanostatic experiments was calculated per gram of organic molecules and it is denoted in figures. Batteries with organic molecules were cycled between 2.0 and 4.0 V versus metallic lithium. Cyclovoltammetry measurements were performed in a two electrode cell with a scan rate being 0.1 mV s^{-1}, if not denoted different.

A LiFePO$_4$ electrode composite containing 3 wt.% of carbon black and 10 wt.% of PTFE as a binder was used for the experiment with **MB** dissolved in the electrolyte. Typical loading of the electrodes was between 4.0 and 4.5 mg cm^{-2}. A glass wool separator was used,
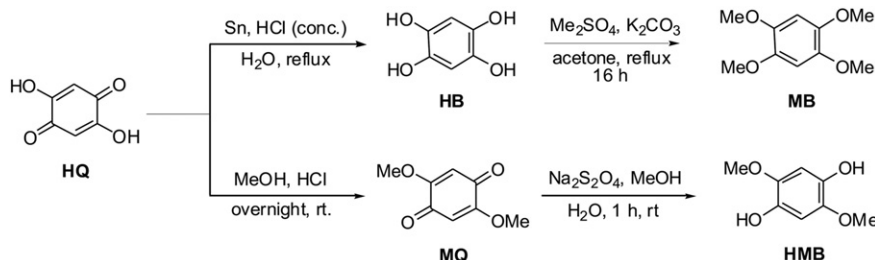

Fig. 1. Schematic of reaction procedures for the preparation of different derivatives of 1,2,4,5-tetrahydroxybenzene.
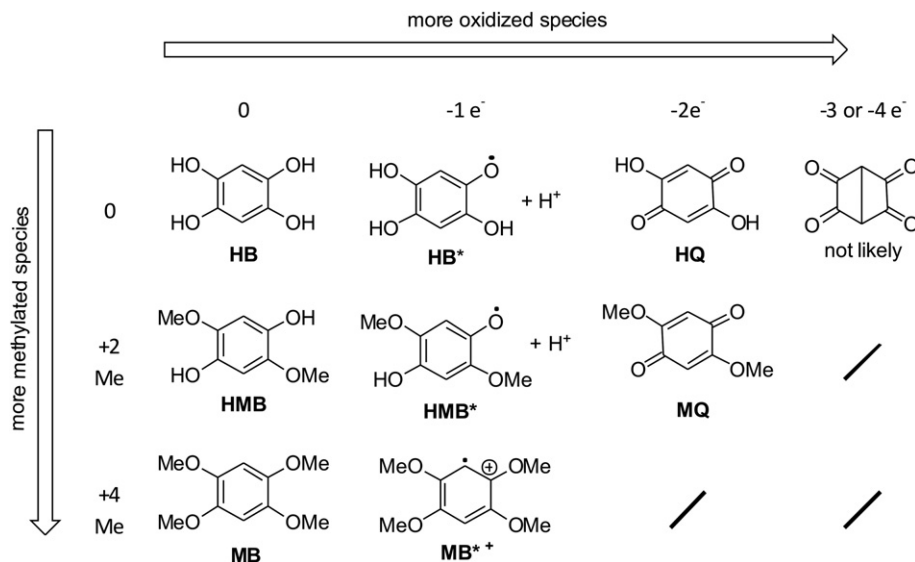
more oxidized species

Fig. 2. Schematic presentation of possible electrochemical reactions between prepared samples used in this study.

soaked with 6 drops (130 mg) of mixture (electrolyte + **MB** = 95/5 (w/w)). The electrolyte was 1 M LiPF$_6$ in EC/DEC = 1:1. Then a conventional coffee bag battery was made using lithium as anode. The current density used in the experiment was equivalent to the C/3 rate based on the mass of LiFePO$_4$.

3. Results and discussion

Five different end products were isolated according to the reaction schemes shown in Fig. 1. All of them were analysed with NMR that confirmed their purity (not shown). Schemes of potential electrochemical reactions between reduced and oxidized derivatives of

quinone are shown in Fig. 2. **HB** (1,2,4,5-tetrahydroxybenzene) and its oxidized counterpart **HQ** (2,5-dihydroxy-1,4-benzoquinone) can exchange two electrons between the reduced and oxidized state. No further oxidation can be expected due to the limitation of the **HQ** molecule which cannot accept any electron without change in the chemical structure (unfavourable). We tested the electrochemical activity of **HB** and **HQ** molecules in a Li-ion battery environment by using cyclovoltammetry measurements. Two major differences between the cyclovoltammograms were observed. One was the irreversible reaction that occurs during **HB** (the molecule with 4 hydroxy groups) oxidation in the first cycle (Fig. 3a). The origin of irreversible charge consumption is not entirely clear but most probably it can be
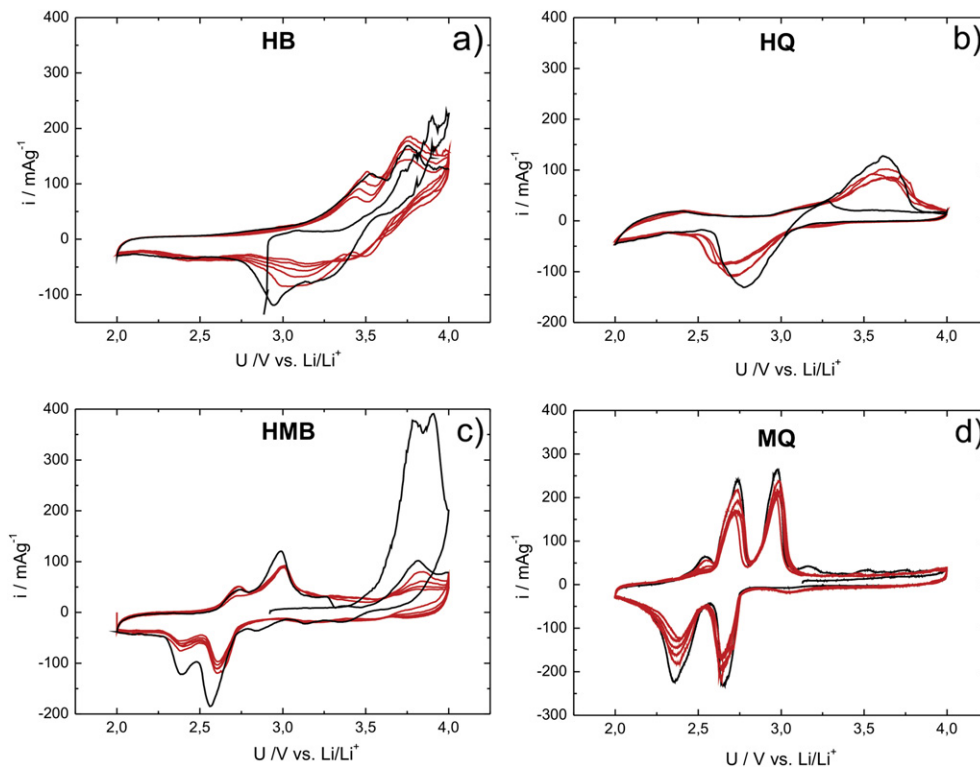

Fig. 3. Cyclovoltammetry scans in first 5 cycles for samples with redox activity, a) for **HB** molecules, b) for **HQ** molecules, c) for **HMB** molecules and d) for **MQ** molecules. Measurements started with oxidation. Black curve corresponds to the scan in the first cycle and during second oxidation.
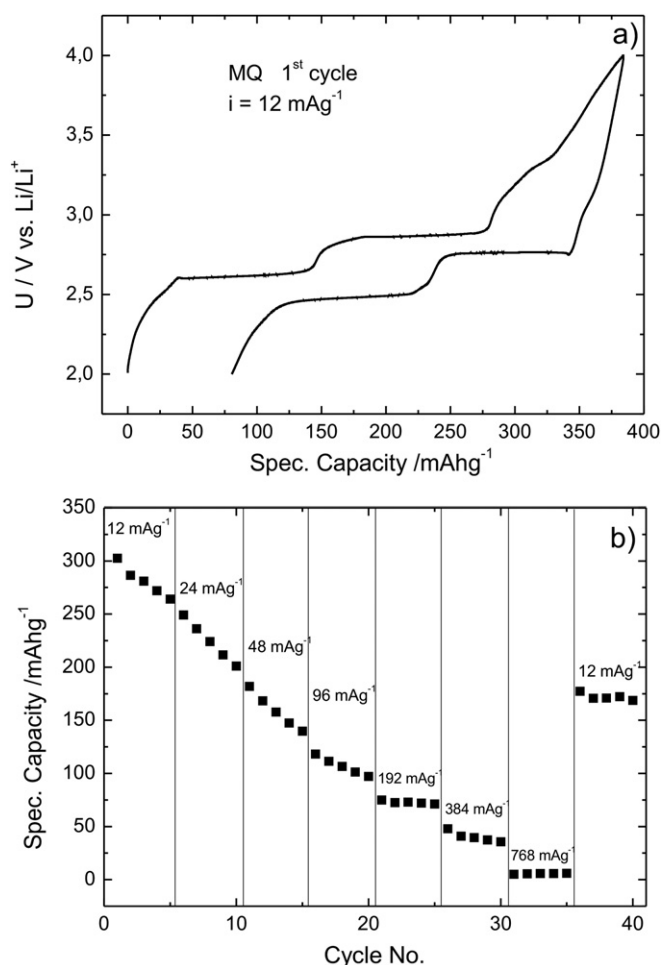
Fig. 4. a) Galvanostatic curve in the first cycle obtained with **MQ** molecules and b) cycling behaviour with different current densities for the battery with **MQ** molecules as active material.

ascribed to the reaction between the electrolyte and the hydroxyl groups since irreversibility was mostly found to take place in the first cycle. By contrast, when **HQ** (dihydroxy quinone) was used no irreversible anodic peak was detected during the first oxidation close to 4 V versus lithium reference and the amount of total irreversible charge was much lower (Fig. 3b). The second difference observed from cyclovoltammograms was their electrochemical activity. The intensity of anodic and cathodic peaks in cyclovoltammograms faded much faster in the case of **HB** molecules if compared to **HQ** molecules. Besides the irreversible reaction, the main reason for the activity fading was also the faster dissolution of molecules with 4 hydroxyl groups compared to the molecules with 2 hydroxyl groups. The redox activity of organic molecules (redox potential and capacity fading) can be changed by appropriate substitution of groups. We selected methylation of hydroxy groups in both **HB** and oxidized **HQ** compounds according to the scheme in Fig. 1. 2,5-Dimethoxy-1,4-benzoquinone (**MQ**) and 1,4-dihydroxy-2,5-dimethoxybenzene (**HMB**) molecules are capable to exchange 2 electrons during oxidation/reduction (Fig. 2), while fully methylated 1,2,4,5-tetramethoxybenzene (**MB**) molecules have no possibility for 2 electrons redox reaction and only 1 electron radical reaction can be expected, as shown in Fig. 2. The electrochemistry of **MQ** was already published before [1,7], however, we wanted to compare it with its reduced compound **HMB** (and with other analogues: **HB**, **HQ** and **MB**). The electrochemical activity of all three samples was tested in terms of cyclovoltammetry measurements. Similarly as in the case of **HB** molecules also **HMB** molecule showed large irreversibility during first oxidation. The formation of irreversible anodic peak at 3.8 V versus lithium metallic reference was present in subsequent scans, however with a fading intensity (Fig. 3c). Methylated molecules (**MQ** and **HMB**) showed a redox activity at lower voltage compared to the non-methylated molecules (**HQ** and **HB**). Both measured methylated samples show a redox activity involving a two-step electrochemical reaction which corresponds to the two electron redox reaction proposed in Fig. 2. Similarly as observed with non-methylated samples, also the more reduced **HMB** molecule (benzene with two methoxy and two hydroxy groups) showed large irreversibility during the first oxidation. We observed as well a small shift in the position of
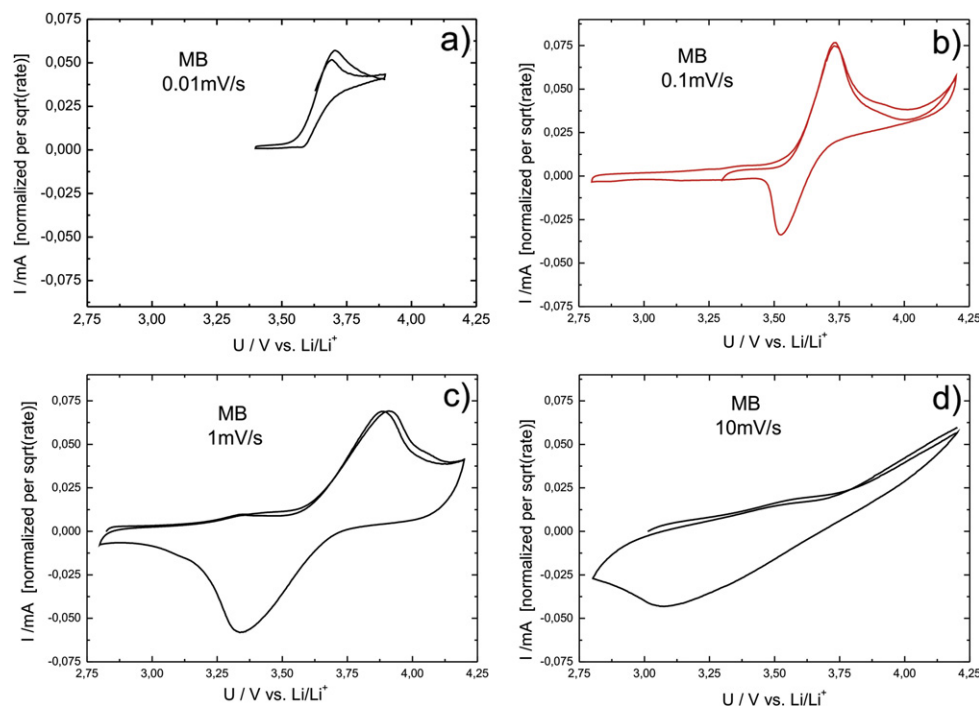

Fig. 5. Cyclovoltammetry scans in first cycle and second oxidation for **MB** molecules obtained with different scan rates: a) 0.01 mVs^{-1}, b) 0.1 mVs^{-1}, c) 1 mVs^{-1} and d) 10 mVs^{-1}.

cathodic and anodic peaks in the cyclic voltammograms. Quinone **MQ** showed a positive shift of approximately 50−100 mV of both the anodic and the cathodic peak when compared to the **HMB** sample. In the **MQ** sample the position of anodic peaks was found at 3 V and 2.7 V while the cathodic peaks were at 2.6 and 2.35 V. Characterisation of the **HMB** sample showed the position of anodic peaks at 3.1 V and 2.85 V, while the cathodic peaks were at 2.65 and 2.4 V. As regards the electrochemical activity, **MQ** molecules shows a significantly better behaviour than **HMB**, both in reversible peaks intensity as well as in almost negligible irreversibility during first oxidation. Galvanostatic cycling of **MQ** molecules showed two reversible redox processes occurring at 2.85 V/2.6 V during oxidation and at 2.75 V/2.5 V during reduction (Fig. 4a). Additional ill-defined plateau was observed during oxidation between 3.13 and 3.3 V in the formation cycle but its origin is not clear at the present stage of research. The obtained capacity in the first cycle corresponds to the utilisation of 94% of the redox active organic molecules (if we consider a 2 electron reaction). The capacity fading during cycling is consistent with the hypothesis of dissolution of active material into the electrolyte solution (Fig. 4b). Interestingly, after about 20 cycles (in our testing procedure this corresponded to a current density of 192 mA g^{-1} or a C/2 cycling rate), the capacity fading more or less stopped. Upon returning to the initial current density of 12 mA g^{-1} (after 35th cycle) the capacity had a value of about 170 mAh g^{-1}, i.e., about 56% of the reversible capacity observed in the formation cycle. The improved stability after a certain number of cycles could be attributed to the saturation of electrolyte with dissolved organic molecules which stopped their further dissolution. This phenomenon confirmed, once again, the importance of stabilisation of redox active organic molecule, for example via their immobilisation by grafting onto insoluble substrate, or by using electrolytes where they have limited solubility [18,19].

Complete methylation of 1,2,4,5-tetrahydroxybenzene (**HB**) resulted in 1,2,4,5-tetramethoxybenzene (**MB**) molecules. According to the structure, **MB** molecules have no redox active centre, thus only radical activity can be expected. Their electrochemical activity was tested by cyclic voltammetry measurements, however, in this case with different scan rates to fully determine their potential use. Fig. 5 shows cyclic voltammograms obtained at scan rates as slow as 0.01 mV s^{-1} up to the relatively fast scan rate of 10 mV s^{-1}. At the slowest scan rate (Fig. 5a) only anodic peak at 3.7 V was detected. Due to the formation of radical cation (according to the mechanism proposed in Fig. 2) the used scan rate was obviously too slow. Namely, the radical cation is attracted by the negative electrode, to which it gradually migrates and reduces back to the neutral molecule **MB**. Consequently, during the reduction half cycle no charge consumption was observed at slow scan rates since the diffusion/migration and reduction processes were faster than the scan rate. Upon increasing the scan rate for one decade to 0.1 mV s^{-1} a reversible cathodic peak occurred (Fig. 5b). A further increase of the scan rate to 1 mV s^{-1} led to even higher activity during cathodic scan (Fig. 5c), however, with a larger potential gap between the anodic and cathodic scan which reflects the kinetic limitations of organic molecules. At a scan rate of 10 mV s^{-1} the activity drops due to the interplay of very large polarisation and limited potential window (Fig. 5d). Galvanostatic cycling of **MB** molecules (Fig. 6) in lithium ion battery environment followed the pattern observed in cyclovoltammetric measurements. At the lowest current density (in our case 6 mA g^{-1}), the galvanostatic oxidation showed a large excess of charge used for the oxidation over the charge used for the reduction (in fact, negligible charge was obtained during the reduction half cycle). Increasing the current density improved the efficiency and led from an almost completely irreversible electrochemical reaction to a fully reversible system at sufficiently high current densities: at 96 mA g^{-1} the
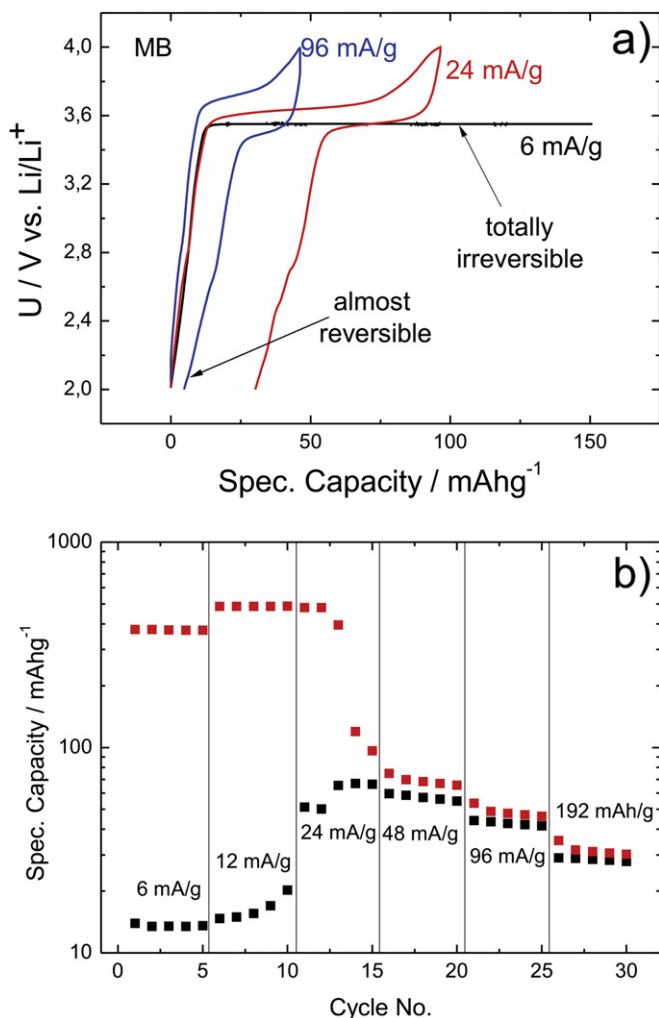

Fig. 6. a) Galvanostatic curves for **MB** molecules measures with different current densities and b) cycling behaviour with different current densities for the battery with **MB** molecules as active material.

efficiency was close to 1. By analogy to the CV results, at low current densities the radical cation is attracted by the negative electrode and if its transport is faster than the cycling rate, the active species cannot act as a charge storage material. A possible solution is fast continuous charging which offers an attractive potential around 3.6 V.

The above results demonstrate how small modifications in the organic molecules can change their electrochemical properties. The particular electrochemical properties of **MB** molecules suggest their potential use as redox shuttle molecules, similar to those investigated in the past for the overcharge protection or for effective determination of the end of charge [8−12]. As mentioned, the potential of radical reaction for **MB** molecules was found to be around 3.6 V versus metallic reference which corresponds well to the end of charge for the LiFePO$_4$ cathode material. To test the suitability of **MB** molecules as a redox shuttle system we prepared a 5 wt.% solution of **MB** in EC:DEC 1 M LiPF$_6$ electrolyte. The amount of electrolyte with **MB** molecules used in all our experiments was adjusted to give a theoretical capacity of **MB** molecules above 100 mAh g^{-1}. Fig. 7 shows galvanostatic cycling of LiFePO$_4$ electrodes where the electrolyte contained **MB** molecules. The cycling rate was C/3 as calculated based on the active mass of LiFePO$_4$ in the electrode (typically from 4 to 5 mg cm^{-2}). Two types of redox
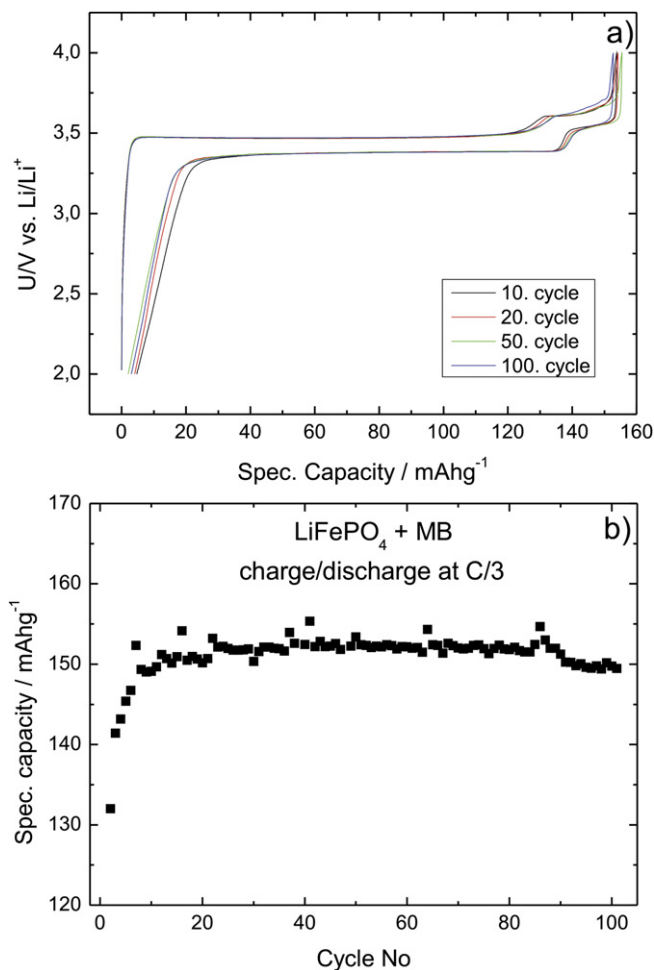
Fig. 7. a) Selected cycles from LiFePO$_4$ based half-cell that contained dissolved **MB** molecules in the electrolyte (5 wt.%) and b) related stability of capacity over 100 cycles.

processes were observed. The first one appeared at 3.45 V versus metallic reference which corresponds to the Fe^{III}/Fe^{II} redox couple in LiFePO$_4$. The second redox couple had its origin in the radical reaction of **MB** molecules with the effective redox activity close to 3.6 V. Since the battery showed in Fig. 7 was cycled at a relatively high cycling rate (a C/3 rate), the redox activity of **MB** molecule was reversible in the continuous cycling mode. The additional charge obtained due to the radical reaction corresponded to approximately 20% of the theoretical capacity of **MB** molecules dissolved in electrolyte. More importantly, half-cells with LiFePO$_4$ and **MB** dissolved in the electrolyte showed excellent cycling stability over 100 cycles (Fig. 7b) pointing out at a good reversibility of **MB** molecules and its stability. Increase of capacity in the first ten cycles was observed in previous study [20] and it is a property of LiFePO$_4$ material used in this experiment. These results support the potential use of 1,2,4,5-tetramethoxybenzene as a redox shuttle system in LiFePO$_4$ batteries as an overcharge protection at the end of the charge.

4. Conclusions

Five oxidized and/or methylated derivates of 1,2,4,5-tetrahydroxybenzene were tested as active materials for potential use in Li-ion batteries. Methylated molecules (**HMB** and **MQ**) showed a redox activity at lower voltage compared to the non-methylated molecules (**HB** and **HQ**). On the other hand, both oxidized samples (**HQ** and **MQ**) showed significantly less irreversibility and better electrochemical stability, obviously due to absence of reactive hydroxyl groups. Galvanostatic cycling of the most promising **MQ** molecules showed two reversible redox processes occurring at 2.85 V/2.6 V during oxidation and at 2.75 V/2.5 V during reduction. The initial capacity is close to the theoretical value (94%) for a two electron reaction but fades to about 50% of the theoretical value after about 20 cycles. After that the capacity is stabilised, most probably due to the saturation of electrolyte with dissolved organic molecules.

Somewhat surprisingly, also the completely methylated quinone (1,2,4,5-tetramethoxybenzene (**MB**)) showed electrochemical activity, although **MB** molecules have no redox active centre. Thus the origin of observed capacity is the radical activity of this molecule. However, this kind of activity displays unusual dependence on the charge/discharge rate: at slow rates no activity is observed during the reduction half cycle because the radical cation is attracted to the negative electrode and reduced back to the neutral molecule. At high enough rates, this diffusion of cation is too slow and good reversibility is observed. It was shown that this kind of behaviour can be used as a redox shuttle for overcharge protection of a LiFePO$_4$ cathode material.

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